

(19) JAPANESE PATENT OFFICE (JP)

(11) Japanese Laid-Open Patent Application (Kokai) No. 59-24244 ✓

(12) Official Gazette for Laid-Open Patent Applications (A)

(51) Int. Cl.³: Classification Symbols: Internal Office Registration Nos.:

G 01 N 27/30

F 7363-2G

(43) Disclosure Date: February 7, 1984

Number of Inventions: 2

Request for Examination: Not yet submitted

(Total of 4 pages [in original])

(54) Title of the Invention: Field Effect Transistor Type of Multi-Ion Sensor, and
Method for Manufacturing Same

(21) Application No. 57-133686

(22) Filing Date: August 2, 1982

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SPECIFICATION

Title of the Invention

Field Effect Transistor Type of Multi-Ion Sensor, and Method for Manufacturing Same

Claims

1. A field effect transistor type of multi-ion sensor, in which a plurality of ion-selective insulated gate field effect transistors are formed on a substrate, wherein said multi-ion sensor is characterized in that n type silicon drain and source components are formed in the surface layer component of p type silicon in the form of wells or islands, a plurality of sensor units are formed on said substrate by covering the upper portion with an oxide film and an insulating film, and at least one comparison electrode-use gate film and a plurality of ion selective electrode-use gate films are formed for each individual sensor unit.

2. A method for manufacturing a field effect transistor type of multi-ion sensor, characterized by comprising:

a first step in which a plurality of p type silicon wells or p type silicon islands are formed on a substrate composed of silicon or sapphire;

a second step in which drain and source components composed of n type silicon are formed in the surface layer component of said p type silicon;

a third step in which sensor units are formed by covering the upper portion with an oxide film and an insulating film after the formation in said second step;

a fourth step in which a liquid produced by dissolving a macromolecular film material having no ion selectivity in a suitable volatile solvent, or a liquid produced by dissolving at least an ion-selective substance and a macromolecular film material in a suitable volatile solvent, is adjusted by use of a nozzle to a droplet diameter corresponding to the sensitive gate of each individual sensor unit, and is sprayed directly onto said gate component, or is sprayed onto said sensitive gate via a mask material having openings at locations corresponding to said sensitive gate component; and

a fifth step in which said solvent is evaporated after the spraying in the fourth step, thereby forming a single comparison electrode-use gate film and a plurality of ion selective electrodes.

Detailed Description of the Invention

The present invention relates to an ion sensor that makes use of field effect transistors (hereinafter referred to as FETs), and more particularly a multi-ion sensor, and to a method for manufacturing this sensor.

Ever since Bergeld established the principle behind them, ion sensors that make use of FETs have undergone continual development to allow the selective detection of a

variety of ions. These ion sensors are made by coating an sensitive gate with an ion selective film. Known methods for coating an sensitive gate with an ion selective film composed of an organic material include dip coating and direct casting (U. Oesch, S. Caras, and J. Janata: Field Effect Transistors Sensitive to Sodium and Ammonium, *Anal. Chem.*, 1981, 53, 1983-1986). CVD (chemical vapor deposition) or dip coating is used as the method for applying an inorganic material.

In all of the examples reported up to now, one or two FET gates are formed on a substrate, and one ion sensitive gate is formed. Consequently, when a conventional method for forming an ion sensitive gate is employed for a multi-sensor having a plurality of sensitive gates on a single common substrate, it is difficult to keep each gate isolated from the others so that they do not interfere with each other.

An object of the present invention is to provide an FET multi-ion sensor in which a plurality of gates formed on a common substrate are coated with an ion selective film so that there is no overlap, and there is no mutual interference, and to provide a method for manufacturing this sensor.

With the present invention, an ion-sensitive substance is dissolved in a suitable solvent along with a film matrix, and the resulting liquid is made into droplets having a small diameter and sprayed onto the desired gate by ink jet method, which results in only a microscopic portion being coated with a sensitive film, after which this coating is repeated, but with the type of ion-sensitive substance varied, which forms a plurality of independent sensitive gates.

A working example of the present invention will now be described.

Figures 1 to 3 illustrate a single FET sensor that serves as a constituent unit of a multi-sensor. When a plurality of sensitive gates are formed on a common substrate, the various elements must be electrically independent from one another. In view of this, the following element structure is adopted in the present invention.

As shown in Figure 1, a sensor unit 2 has been formed on a common substrate 1, and a lead wire 4 and a contact 5 have also been formed on the substrate by vapor deposition or another such method. The size of the sensor unit is about $50\text{ }\mu\text{m} \times (200\text{ to }400)\text{ }\mu\text{m}$. As shown in Figure 2, when p silicon is used for the common substrate, the FET gate portion is dug out and an insulating film 7 is formed, after which another silicon p layer 13 is formed. After this, an n layer 8 is formed by diffusion in order to form a drain and a source. The upper portions of the drain and source are coated with an oxide film layer 9, an insulating film layer 10, and an ion selective film 11 to produce a sensor unit.

Figure 3 illustrates a sensor unit having a silicon-on-sapphire (SOS) construction. The common substrate 12 is sapphire, on the upper portion of which a p silicon layer 7 is formed by epitaxial growth. The drain and the gate 8 are formed by diffusion, and the upper portion thereof is coated with an oxide film layer 9, an insulating film layer 10, and an ion selective film 11 in the same manner as in Figure 2.

Figure 4 illustrates a multi-ion sensor in which four of the sensor units produced by the above method have been formed on a common substrate. The first unit 21 has a

comparison electrode-use gate 22. This gate is coated with an organic macromolecular film that does not respond to ions and the like. The gates of the other sensor units 23, 25, and 27 are each coated with an ion selective film that responds to a different ion.

Figure 5 illustrates the method in the present invention for applying the ion selective films. This method used to be employed in ink jet printers, and involves the intermittent spraying of droplets 45 from a nozzle 44, which pass through charging electrodes 46, and then are sprayed out from between deflecting electrodes 47. Usually, a voltage is applied in advance to the charging electrodes 46 and the deflecting electrodes 47, and the droplets are guided by a gutter 48. The voltage applied to the charging electrodes 46 is cut off in pulses, and the droplets are guided to the desired gate on the substrate. Here, a mask material 40 having a small-diameter opening 41 may be used in order to prevent malfunction of the apparatus. The solvent is evaporated off to form an ion selective film.

The inventors of the present invention fabricated a multi-sensor comprising a substrate with a diameter of 1.5 mm. The size of the sensor units was $50\text{ }\mu\text{m} \times 300\text{ }\mu\text{m}$, and that of the gate portions was $50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$. As shown in Figure 4, four sensor units and one gold electrode 29 were formed on this substrate. Gate films were formed using the organic film application apparatus shown in Figure 5. A polyimide-amide resin was used as the sensitive film for the comparison electrode, and this resin was dissolved in dimethylformamide, and the resulting liquid was put inside the vessel 42 shown in Figure 5. The substances used for the various ion selective films were K^+ electrode-use valinomycin, Na^+ electrode-use *gokan*¹ ligand, and Cl^- electrode-use quaternary ammonium salt, each of which was used in the form of a liquid obtained by dissolving the respective substance in tetrahydrofuran along with a plasticizer and polyvinyl chloride (PVC). The diameter of the nozzle from which the droplets were sprayed was $25\text{ }\mu\text{m}$. An ultrasonic oscillator 43 was used to spray the droplets, and the ultrasonic oscillator was ordinarily actuated continuously. Each solution was sprayed onto the gate by cutting off the voltage of the charging electrodes in pulses, and the film thickness was adjusted by varying the number of times the solution was sprayed. Since a single droplet spreads out to a diameter of approximately $50\text{ }\mu\text{m}$ on the gate, the number of droplets was one to three, and the spread of the film over the gate was no more than $100\text{ }\mu\text{m}$. After the application of the droplets, the solvent was evaporated at room temperature to form a sensitive film.

With the method for applying the sensitive gates given in this working example, it is possible to form ion selective films and a comparison electrode film on just the desired gates, and to form a different type of ion sensor on each gate. Therefore, the selectivity of each ion sensor is the same as when it is formed on a substrate by itself. It is also possible to control the film thickness by means of the number of droplets sprayed, and to produce a multi-ion sensor with good reproducibility.

¹ Translator's note: This term could not be found by this or two other translators. The characters literally mean "meet-feel." It seems highly likely that this is a typo. Possibly, it might be *ketsugo* meaning "bonding," or *kango* meaning "engaging."

As described above, the present invention allows a plurality of gates formed on a common substrate to be coated with ion selective films such that there is no overlap, so there is no interference among the gates.

Brief Description of the Drawings

Figure 1 is a diagram of the principle involved in the present invention;

Figures 2 and 3 are diagrams illustrating a working example of the present invention;

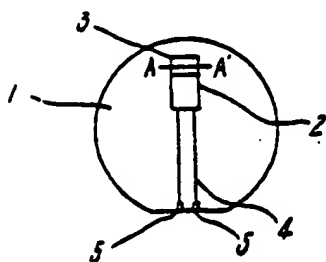
Figure 4 is a diagram illustrating a working example of a multi-ion sensor; and

Figure 5 is a diagram illustrating the gate formation method.

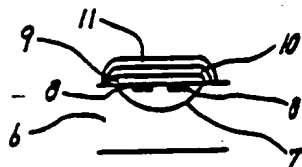
Key: 1 substrate, 2 sensor unit (FET), 3 sensitive gate, 4 lead, 5 contact, 6 p silicon substrate, 7 is an insulating film, 8 drain and source, 9 oxide film, 10 insulating film, 11 ion selective film, 12 sapphire substrate, 13 p silicon, 21 comparison electrode unit, 23, 25, and 27 ion sensor units, 22 comparison gate, 24, 26, and 28 ion sensitive gates, 29 gold electrode

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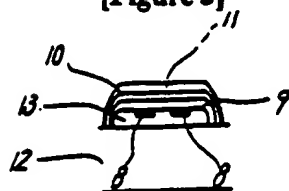
[Figure 1]



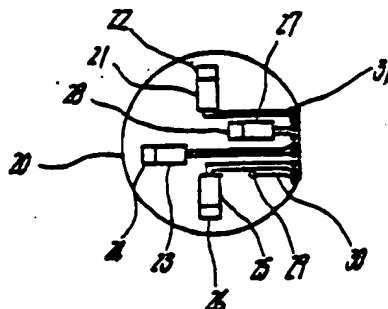
[Figure 2]



[Figure 3]



[Figure 4]



[Figure 5]

